



Electrodeposition of Nanocrystalline Cobalt Phosphorous Coatings as a Hard Chrome Alternative

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Inorganic Coatings SME

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Report Documentation Page

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Project Team

NAVAIR: NAVAAIR



- PI: Ruben Prado, NAVAIR JAX
- Co-PI: Jack Benfer, NAVAIR JAX

Robert Kestler	NAVAIR CP - Requirements and Demonstrations across NAVAIR programs and OEM
Mike Firth	NAVAIR LK - Ground Support Equipment requirements and components
Steve Brown	NAVAIR PAX - Test requirements and Qualification, JTP
Denise Aylor	NAVSEA - Leveraged Effort, NAVSEA Systems Requirements, Mil-Spec development

Integran Technologies:



- Neil Mahalanobis, Constantine Collias
 Integran Technology Development & Optimization, Dem/Plan
- Keith Legg, Rowan Technology Group, Libertyville, IL, -- CBA, reports, Implementation Assessment, ASETSDefense website



Technical Objectives

- Demonstrate/Validate pulsed electrodeposition of Nanocrystalline Cobalt-Phosphorous (nCoP) alloy coatings as a Hard Chrome (EHC) electroplating alternative for DoD manufacturing and repair.
 - Fully define deposition parameters and properties
 - Establish production plating processes (i.e., cleaning, racking, masking, activation, pre-plates, stripping, etc.)
 - Demonstrate/Validate performance
 - Develop Eng Tech Data Packages
 - Manuals
 - Specifications
 - Eng. Circular
 - Transition Package
 - Initiate DoD and OEM approval process



Demo Site: FRC JAX



Technology Description

(nCoP Pulsed Electrodeposition)

Coating applied by electrodeposition

- **Pulsed Current Waveform Engineering**
 - Frequency (Hz) = $1/(t_{op}+t_{off}) = 25Hz$
 - Duty Cycle (%) = $t_{op}/(t_{op}+t_{off})x100 = 50\%$

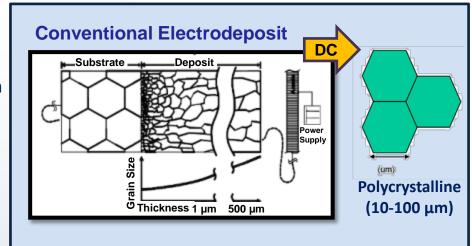


Electrodeposited nanocrystalline materials

- *Favors nucleation of new grains over growth
- Results in an ultra-fine grain structure
- Uniform throughout thickness

Leads to unique properties

- ↑ Yield Strength, wear, ultimate tensile strength
- ↑ Density
- ↓ Coefficient of friction



^{*}Smaller grain size impedes dislocation movement and increases yield strength

Nanocrystalline Electrodeposit Pulse *Nanocrystalline E Thickness 1 μm (< 100 nm) 500 µm 116 ASF, 50%, 25 Hz *nCoP electrodeposits have grains of ≤20 nm; (hexagonal close-packed (HCP) crystal structure)



Technology Description (nCoP Pulsed Electrodeposition)

Process Comparison

<u> </u>				
	Nanovate™ R3010	EHC		
Deposition Method	Electrodeposition (Pulse)	Electrodeposition (DC)		
Part Geometries	LOS and NLOS	LOS and NLOS		
Efficiency	85-95%	15-35%		
Deposition Rate	0.002"-0.008" /hr	0.0005"-0.001" /hr		
Emission Analysis	*Below OSHA limits	Cr+6		
Bath Temperature	185°F	140°F		



Cathode Efficiency

Approaches 100% Efficiency nCoP Plating 50% Cr Plating ▲ 1800 RPM 1000 3000 Current density [A/m2]

*Co PEL is 20 µg/m3

⚠ Nanovate ™R3010 Plating Tank at FRCSE Temp = $185^{\circ}F$ pH = 1.0 - 1.2

- At least 5X faster than Chrome plating
- Increased throughput
- One nCo-P tank can replace several hard chrome tanks
- Bath is Stable



Technical Approach (Dem/Val Line at FRCSE- Jacksonville)

NAVAIR Fleet Readiness Center Jacksonville

- Dem/Val line in operation since 2006
- 250 gallon Plating Tank
- Pulse Power supply (1500A Peak Current)
- Activation tank used for most all alloys
- CIP # 0466 Established



Process Line



Dem/Val Tank Pulse Power Supply

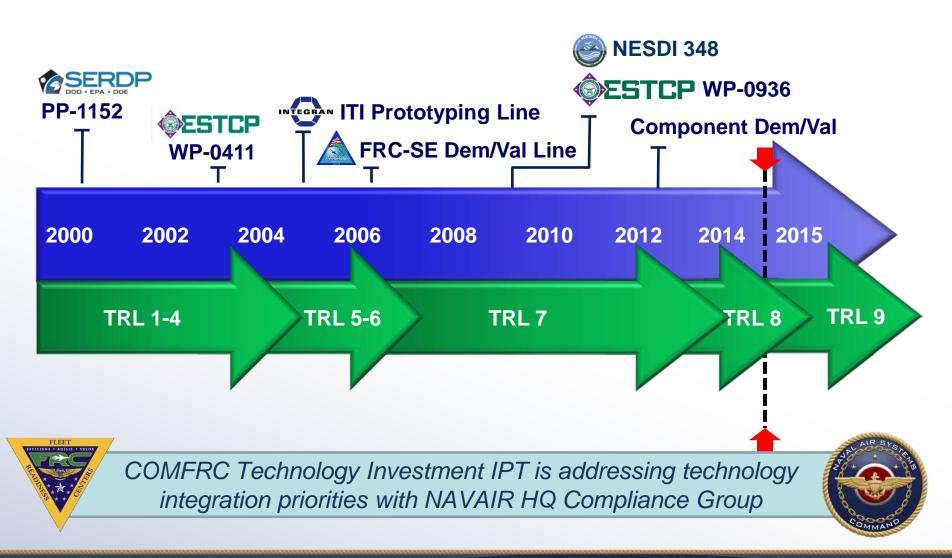


Activation Tank Power Supply



Technology Integration

(Technology Readiness Level)





Joint Test Protocol

(JTP - Demonstration/Validation)

24 Core Tests Defined in JTP

- Appearance ✓
- 13. Corrosion (OCP) ✓

Thickness ✓

14. Adhesion ✓

Porosity ✓

15. HE ✓

Hardness ✓

16. HE (No Bake) ✓

Grain Size ✓

17. Fluid Compatibility ✓

Ductility **✓**

18. HRE ✓

Stress

19. Wear - Taber ✓

Fatigue ✓

- 20. Wear Pin on Disk ✓
- **Coating Integrity** ✓
- 21. Wear Endurance Rig ✓
- 10. Corrosion (B117) ✓ 22. Wear Falex ✓
- 11. Corrosion (SO2) ✓ 23. Wear Gravelometry ✓
- **12.** Corrosion (Beach) ✓
- 24. Wear SATEC ✓

100 % Plating/Testing completed

100% Draft JTR completed

95% Dem/Vals Completed

3 Dem/Vals



T45 Pivot Installed: Mar 2012



Lifting Arm Pin

Installed: Jul 2013



M9ACE Cylinder

Installed: Mar 2014



Performance Criteria/Results

(Joint Test Protocol - Demonstration/Validation)

Engineering Requirement	Test	Acceptance Criteria / Notes	Results
Appearance	Visual examination	Smooth, fine grained, adherent, uniform in appearance, free from blisters, pits, nodules, excessive edge build-up and other defects	Pass
Porosity	Ferroxyl	No pits > 1/32" diameter < 15 pits in 150 sq.in < 5 pits in 30 sq.in.	Pass
		Hardness: nCoP ≥ EHC	Pass on selected heat treatment conditions
Hardness	Vicker's microhardness	Target Hardness > 850 VHN (EHC requirement) nCoP maximum hardness obtained 763 VHN following heat treatment 550°F for 5 hrs.	Fail
		Threshold Hardness > 530 VHN (process requirement)	Pass
		S-N curve fitted data: nCoP ≥ EHC at 0.003"	Pass
Fatigue	Axial Fatigue	S-N curve fitted data: nCoP ≥ EHC at 0.010"	Pass
		S-N curve data fitted: nCoP at 0.010" ≥ Ni+EHC at 0.005" ≥ Ni+nCoP at 0.005"	Marginal Pass



Performance Criteria/Results

(Joint Test Protocol - Demonstration/Validation)

Engineering Requirement	Test	Acceptance Criteria / Notes	Results
Coating integrity	Axial fatigue	The nCoP coatings must not spall or delaminate	Pass
Corrosion	 SO₂ salt fog Beach exposure Neutral Salt Fog 	Average appearance/Protection ranking vs time curve: nCoP ≥ EHC per ASTM B537	Pass
Corrosion	Open circuit potential	No acceptance criteria – for information purposes only	Pass
Adhesion	Bend/chisel ASTM B571 AMS 2460	nCoP does not show separation from the basis metal at the common interface	Pass
Hydrogen embrittlement	BakeNo Bake	1a1: four bars > 200h load to failure: nCoP ≥ EHC	Pass
Environmental Embrittlement	Sustained load in saltwater environment	150 hrs+ and 45% NFS+: nCoP ≥ EHC in DI water nCoP ≥ EHC in Salt water	Pass (DI water)
Fluid compatibility	Visual observation and weight loss following immersion	nCoP must not exhibit chemical attack greater than that exhibited by EHC.	Pass Fails with Chlorine Bleach, Nital Etch & Ammonium Persulfate



Performance Criteria/Results

(Joint Test Protocol - Demonstration/Validation)

Engineering Requirement	Test	Acceptance Criteria / Notes	Results
	Pin on disk	Coating wear volume loss, coefficient of friction, static partner wear volume loss: nCoP ≤ EHC	Pass
	Endurance rig test	< one drop of hydraulic fluid in 25 cycles and acceptable wear (i.e., not affecting leakage performance)	Pass
Wear	Falex block on ring	Coefficient of friction, average weight loss and average wear volume: nCoP ≤ EHC	Pass
	Gravelometry	CoP performance equal to EHC	Pass
	Taber Abrasion	Taber wear index: nCoP ≥ EHC	Fail
	SATEC oscillating load	Coefficient of friction, average bushing wear: nCoP ≤ EHC	Pass

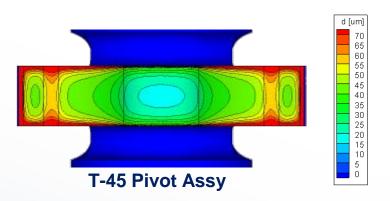


(Overview of Prior Work)



Electrochemical Modeling







Phase I Characterization (JTP) Tests

	Requirement	пСоР	EHC
Appearance	Smooth, uniform, free of pits/defects	Pass Bright & shiny	Pass Dull/Matte
Adhesion	No separation between deposit/substrate	Pass	Pass
Ductility	> 2%	Pass 2.9%	Pass <1.0%
Grain Size	<20 nm (HCP)	Pass 6 nm(HCP)	N/A
Porosity	<1/32", <15 pits/150 in², <5 pits/30 in²	Pass ≤ 1 spot per 30 in²	Pass ≤ 5 spot per 30 in ²



Chemical Strip Demonstrated

Demonstrated on T-45 Pivot at JAX





Plated Pivot

Stripped Pivot



Masking Evaluation/Downselect





MT-1024 by Masktec Inc





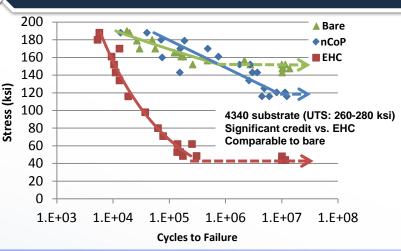




(Overview of Prior Work)

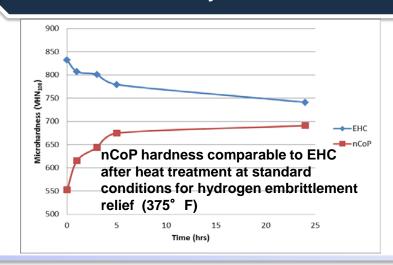


Rotating Beam Fatigue Test





nCoP Heat Treat Study





NAVAIR JAX Base line Plating - Dem/Val



EHC Plating of T-45 Pivot Assy



OSD Coupon Testing Completed



Taber Abrasion, Impact, Adhesion, Corrosion







480 Hrs

720 Hrs

Carburized 1018 Steel Coupons



(Masking evaluation)



High Temp Wax Evaluation/Electroplaters tape

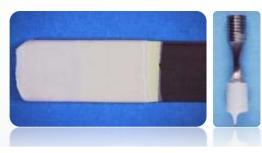
- Root cause of pitting identified from traditional electroplaters tape (breakdown of backing adhesive).
 - High Temp 3M Vinyl Tape Resolved pits
- Evaluating non-solvent based High Temp Wax (Darent Wax Company LTD)
 - Performed Thermal Analysis
 - Compatible with nCoP plating Bath
 - Initial evaluation on small mock-up samples/pieces
 - Melting Point >100 °C (212 °F)
 - Rapid Solidification
 - Ease of Use



Thermal Analysis of Wax



Traditional electroplaters tape (L) and custom electrical tape (R).



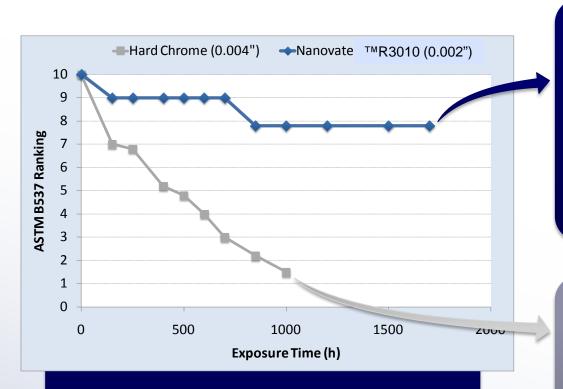
Maskant on Flat Coupons/Threaded items Evaluated at 130°C (266°F)



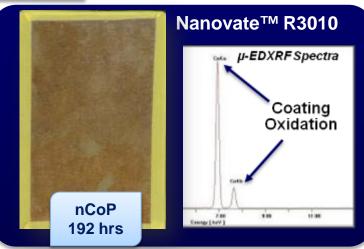
Technical Progress (ASTM B-117 Corrosion Testing)

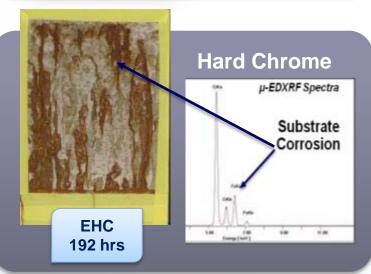


Salt Fog Testing (ASTM B-117)



ASTM B537 Ranking following ASTM B117 Salt Spray







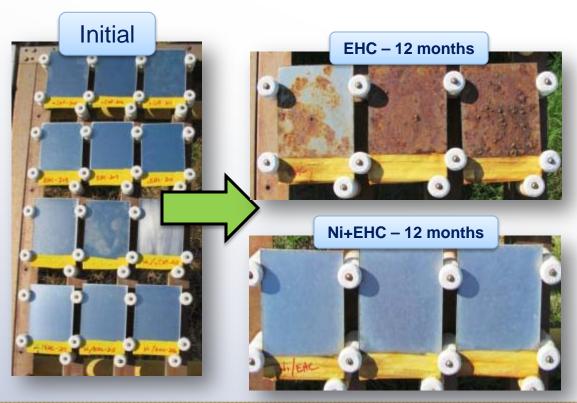
(Corrosion – Beach Exposure)



Kennedy Space Center Beach Exposure

- Beachside Atmospheric Test Facility, NASA KSC
- EHC exhibits red rust
- Discoloration consistent with cabinet testing on nCoP











(OSD Corrosion Testing)

Cycling corrosion/seal wear:

Cylinder Testing Cycle (1 mil coating):

- 1. Cylinder cycling 1000 cycles then
- 2. ASTM B117 10 days

nCoP plated cylinders have completed a cumulative total of 100 days ASTM B117 and 10,000 cylinder cycles with **no reported failure due to seal leakage.**





10,000 cycles/ 100 Days
No Failures





4000 cycles/ 40 Days EHC-2 Failed







(Wear Testing for Shafting Application)

Journal Wear Testing Completed:

- nCoP demonstrated as a viable alternative for Navy propulsion shafting applications
- Wear testing showed no measurable mass loss.
- Evaluated Galvanic, general & Crevice Corrosion
- Demonstrated bond integrity on Inconel 625, 70/30 CuNi & low alloy steels
- Dem/Val on large scale shafts successfully demonstrated under an ONR Swampworks program.



Wear test equipment





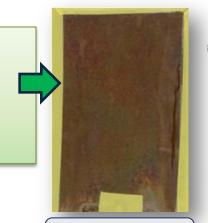
Nanovate™ R3010 Plating on Navy Shaft geometries/materials



(Oxide Characterization)

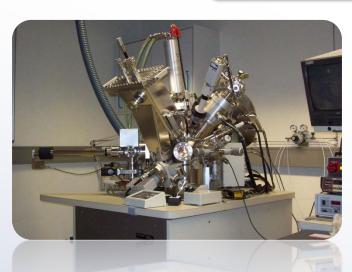
Oxide Characterization Completed

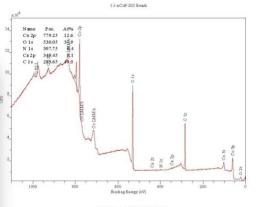
✓ X-ray photoelectron spectroscopy (XPS) analysis determined Co oxide (Co₃O₄) and CoO on surface. (NO IRON PRESENT)



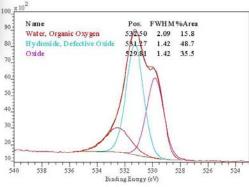
nCoP Coupon (Nanovate R3010)



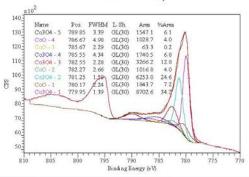








1-1 nCoP-205 B each Co 2p





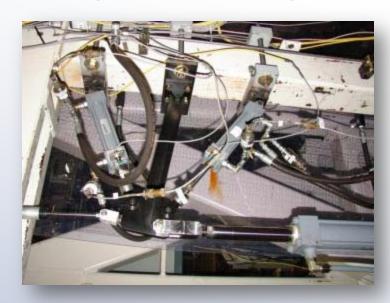
(Endurance Rig Testing)



Endurance Rig Testing

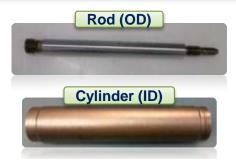
- Assess wear performance vs. chrome as an ID actuator
- Test developed by Messier-Dowty
 - 20,000 Cycles
 - Criteria -- Less than one drop of hydraulic fluid in 25 cycles and acceptable wear
 - Observe effect of surface finish, seal types, and hardening condition

Image of Endurance Rig Test

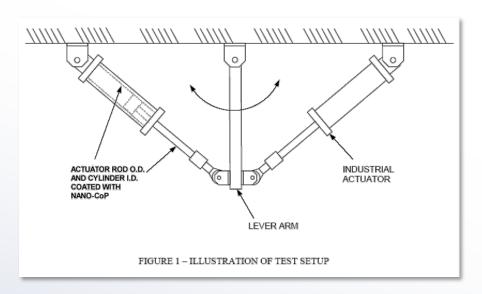




nCoP tested as good or better than EHC



Endurance Rig Test Schematic



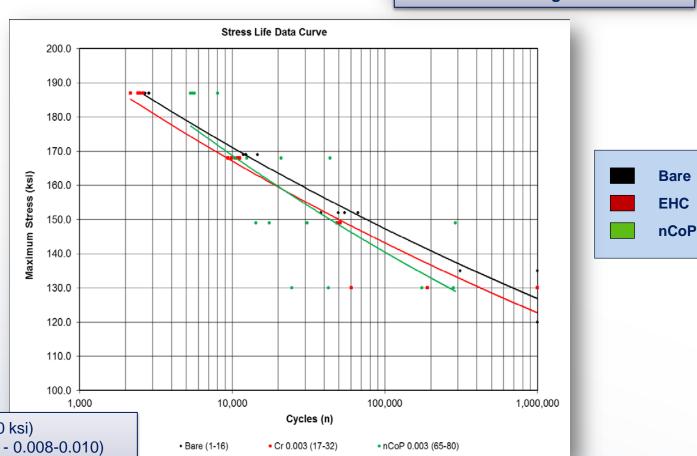


(Fatigue Testing)



Axial Fatigue Testing



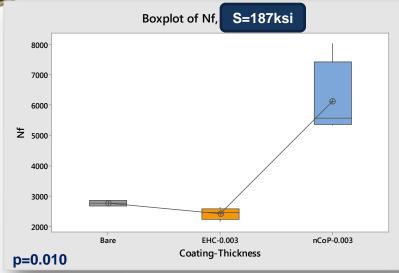


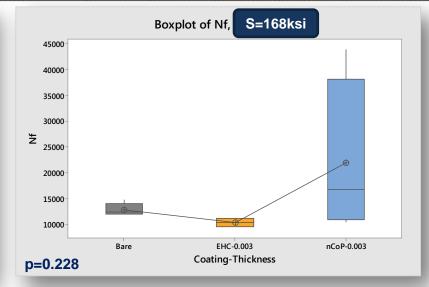
Test Conditions

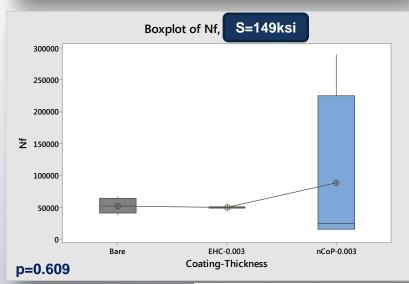
- 4340 steel (260-280 ksi)
- Shot peened (S110 0.008-0.010)
- 16 Ra Minimum
- R ratio: R = -1, Freq: 20 Hz
- Loads: 85% YS to 10⁶ Cycles

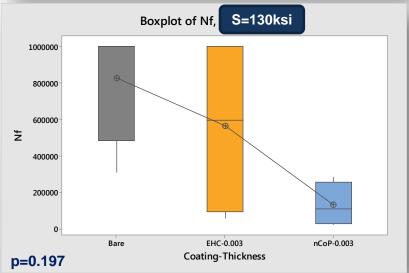


(Fatigue Testing)









Boxplot comparing bare with EHC and nCoP coated samples at a thickness of 0.003" at each load level.



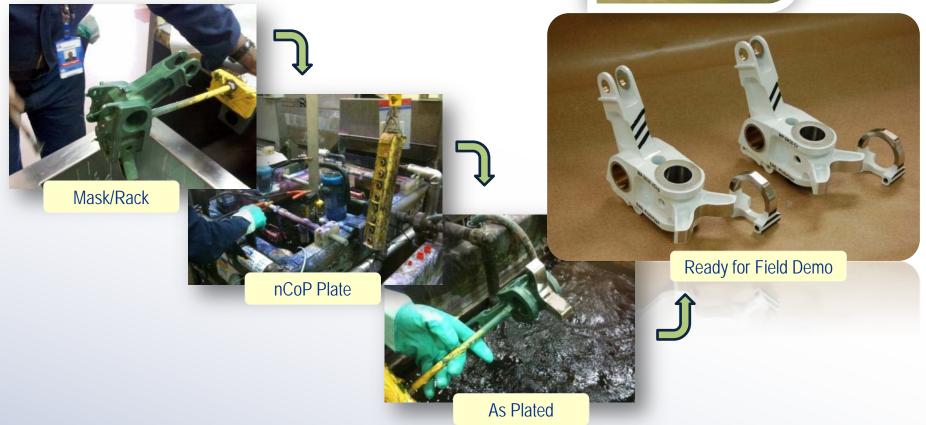
(Component Dem/Val Electroplating Process)



NAVAIR JAX Plating Dem/Val - May 2011

nCoP Plating of T-45 Arresting Hook Pivot







(T-45 Pivot Assy)



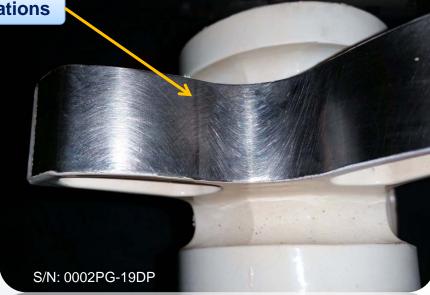
Dem/Val Component Field Inspection

- Field Performance: T-45 Arresting Hook Pivot
 - nCoP plated pivot inspected after 72 & 97 arrestments
 - Passed inspection & reinstalled on A/C
 - 116 arrestments w/ 900 ± 15 Total Flight Hrs as of Nov 2014





nCoP – After 72 arrestments, 705 ± 10 Flight Hrs



nCoP – After 97 arrestments, 825 ± 15 Flight Hrs



(T-45 Pivot Assy)

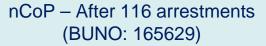


Dem/Val Component Field Inspection

- **Field Performance: T-45 Arresting Hook Pivot**
 - nCoP Plated Pivot reaches 116 Arrestments!
 - Baseline still at 63 Arrestments









EHC – After 63 arrestments (BUNO: 165463)



(M9 ACE Cylinder)



M9 ACE Cylinder Dem/Val

- Assembled/Pressure Tested at Marine Corp Depot, Albany, GA
- Installed on Vehicle Mar 2014
- Field tested at Panama City





Nanovate[™] R3010 plated Hydraulic Cylinder for M9 ACE (Armored Combat Earthmover)





(Lifting Arm Pin)



Dem/Val Component on Carrier (CVN-75)

- Pins installed Jul 2013; Onboard CVN-75 USS Harry S Truman
- >672 A/C moves since installation
- Pins passed 91 day PMS NDI Inspections
- Fleet saving ~2.5 man hrs/pin to clean/prep for NDI
- nCoP coated pins outperformed baseline
- Endorsement Letter provided by cognizant Engineer



Spotting Dolly (A/S32A-32, S/N: QCF137) with Dem/Val pins on carrier

"These pins are a dream to work with; considering no prep work is required for NDI. Hopefully this project leads to all pins, including the adapter pins having this coating."

-- Senior Chief on board the CVN 75



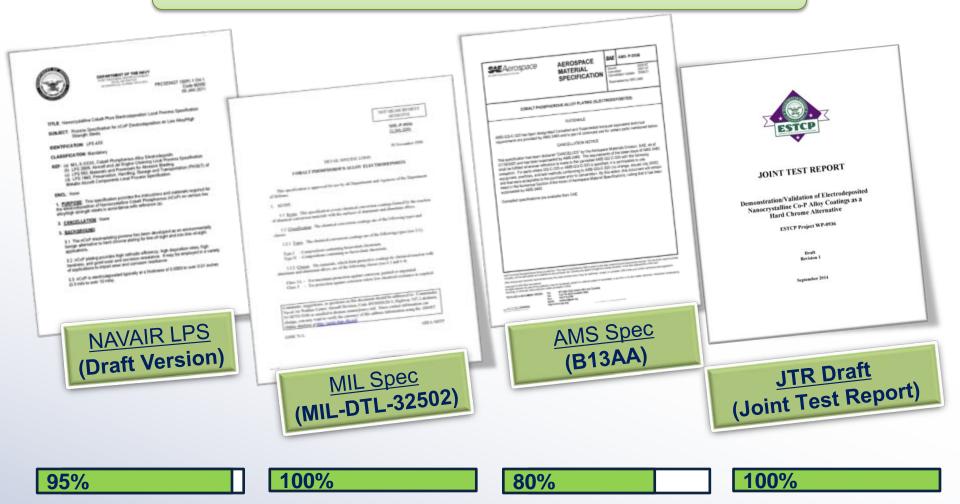
Dem/Val Pin prior to NDI





Technology Transfer

(Specification Development)



Percent Complete



Questions

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Backup Material





Acronyms and Symbols

CDR – Critical Design Review

DOE – Design of Experiment

EDS – Energy Dispersive Spectroscopy

EHC - electrolytic hard chrome

FOC - Full Operating Capability

FRCSE - Fleet Readiness Center South East

HE – Hydrogen Embrittlement

ID - Internal Diameter

ISSC – In Service Support Center

JTP - Joint Test Protocol

LED - Local Engineering Instruction

LOS – Line of Sight

LPS – Local Process Specification

MIPR - Military Interdepartmental Purchase Request

NAVAIR - Naval Air Systems Command

NDI - Non Destructive Inspection

NLOS - Non-line-of-sight

nCoP - nanocrystalline cobalt-phosphorus

OD - Outer Diameter

OSD - Office of the Secretary of Defence

PEO - Program Executive Office

PMA - Program Manager - Air

SEM - Scanning Electron Microscope

SRR - System Requirements Review

μ-EDXRF – Micro energy dispersive X-ray fluorescence



Publications

Papers/Publications Since IPR 2010

D. Facchini, J. McCrea, P. Lin, F. Gonzalez and G. Palumbo, "Microstructural Engineering of Surfaces: Applications for Nanocrystalline and Grain Boundary Engineered Materials in Aerospace and Defense", proceedings of the SURFAIR Conference, Biarritz FR, June 10th, 2010

Prado, R.A., Benfer, J., and Facchini, D., 2011. Electrodeposition of Nanocrystalline Co-P Coatings as a Hard Chrome Alternative. In: ASETS Defense, Sustainable Surface Engineering for Aerospace & Defense, New Orleans LA, February 8-11, 2011.

F. Gonzalez, "Electroplate Alternatives to Hard Chrome: Nanocrystalline Metals and Alloys", proceedings of NASF SUR/FIN 2010, Grand Rapids, MI, June 16th, 2010

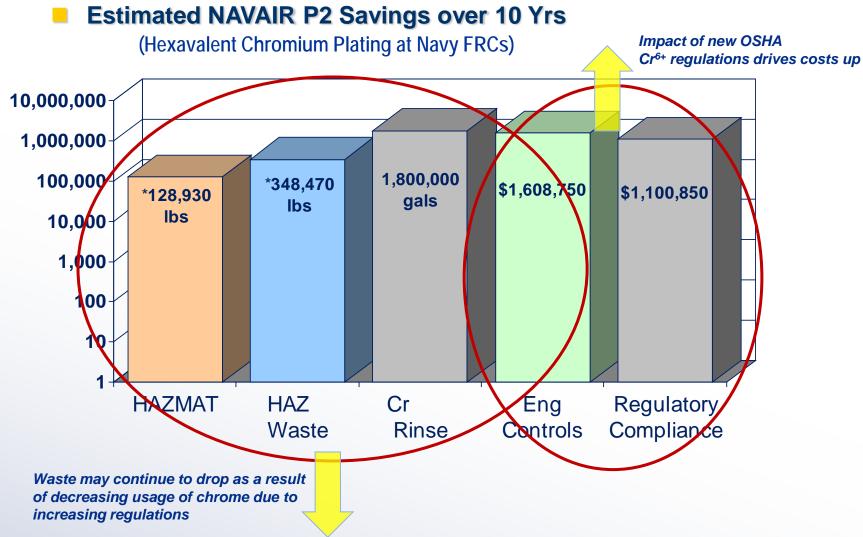
Prado, R.A., Benfer, J., Facchini, D., Mahalanobis, N., Gonzalez, F. and Tomantschger, K., 2011. Electrodeposition of Nanocrystalline Co-P Coatings as a Hard Chrome Alternative for use in DoD Acquisition Programs. To be presented at: NASF SUR/FIN 2011, Chicago II, June 13-15, 2011.

Patents/Patent Applications

U.S.7,910,224 (2011), US 7,824,774 (2010), US 7,320,832 (2008): Fine-grained metallic coatings having the coefficient of thermal expansion matched to the one of the substrate US 5,433,797 (1995): Nanocrystalline metals
US 5,352,266 (1994): Nanocrystalline metals and process of producing the same US 2010/0304182 (2010): Electrodeposited metallic-materials comprising cobalt



Environmental – Cost Benefits



Note: the above projected savings are assumptions based on FRC-SE data extrapolated to other Navy FRCs. Estimated amounts due to chrome plating based on average Environmental Systems Allocation (ESA) data extrapolated across all FRCs over a 10 yr period





Coating Properties (Nanovate™ R3010 vs. EHC)

Property	Test Method	Applicable Standard	Nanovate ™R3010	EHC
Appearance and porosity	Visual and microscopic inspection	N/A	Free from pits, microcracks and pores	Microcracked
Grain Size	X-Ray Diffractometry	N/A	8-15 nm	-
Hardness	Vickers Microhardness	ASTM B578	550-600 VHN (as-deposited)	Min. 600 VHN
			600-750 VHN (heat treated)	-
Ductility	Bend Test	ASTM B489	2-7%	<1%
Adhesive Wear	Pin on Disc (Al ₂ O ₃ Ball)		6-7 x 10 ⁻⁶ mm ³ /Nm	9-11 x 10 ⁻⁶ mm ³ /Nm
Coefficient of friction		ASTM G99	0.4-0.5	0.7
Pin Wear	V 2 - 3		Mild	Severe



Coating Properties (Nanovate™ R3010 vs. EHC)

Property	Test Method	Applicable Standard	Nanovate™ R3010	EHC
Abrasive Wear	Taber Wear (CS-17 wheels)	ASTM D4060	17 mg/1000 cycles	4 mg/1000 cycles
Corrosion	Salt Spray	ASTM B117	0.003" thick Pass 165 hrs 0.002" thick Protection Rating 7 (ASTM B537) @ 1000 hours	0.003" thick Fail 165 hrs 0.004" thick Protection Rating 2 (ASTM B537) @ 1000 hours
Deposit Stress	Internal Stress Test	N/A	10-15 ksi (Tensile)	Cracked – Exceeds cohesive strength
Fatigue	Rotating Beam Fatigue	N/A	Comparable to bare at high loads. Small debit compared to bare at low loads. Credit compared to EHC.	Significant debit compared to bare at all loads.